Today

Reaction Coordinates

Activation Energy

Catalysis

We have a balloon with H_2 and O_2

why is not reacting?

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

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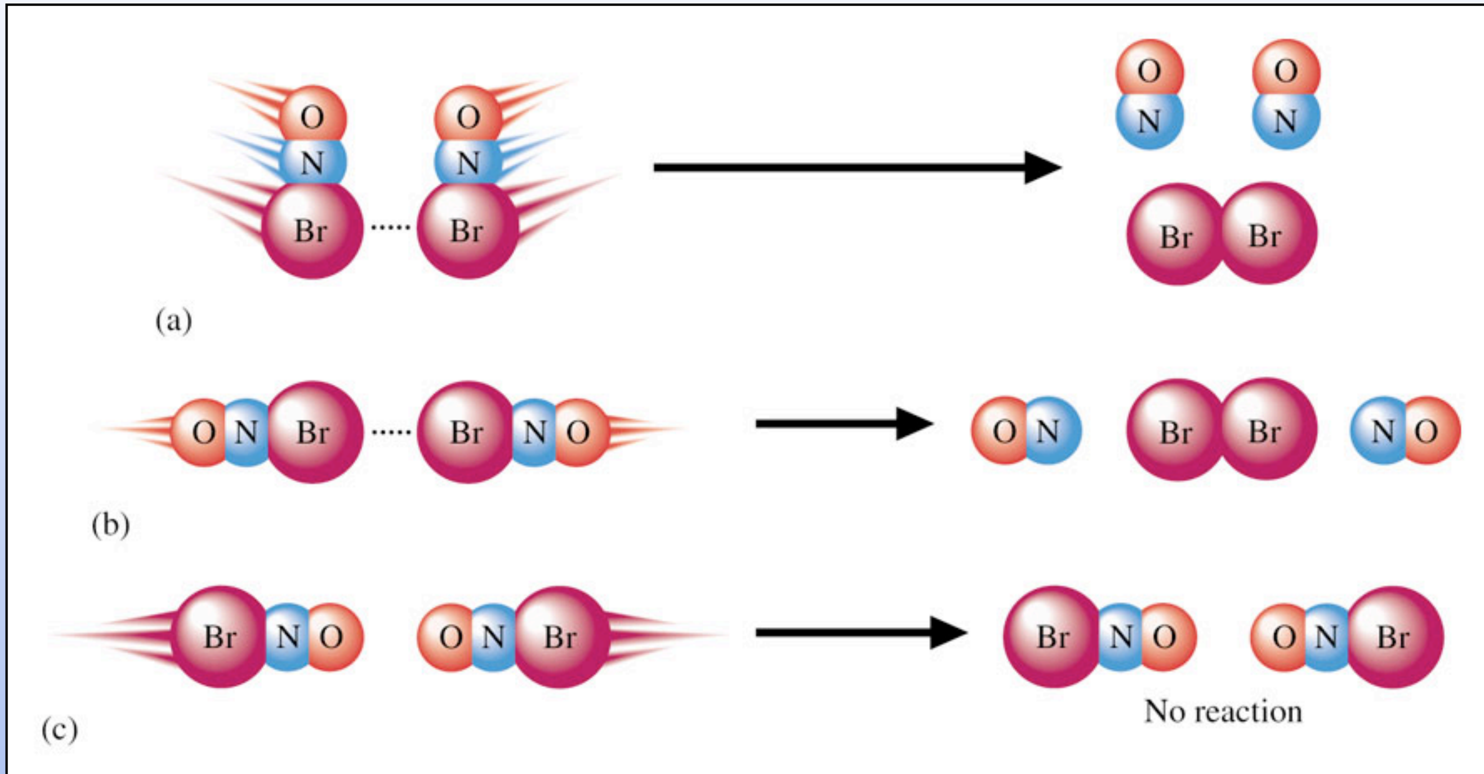
A. this reaction is not spontaneous at room temperature

B. the reaction is very slow at room temperature

C. the reaction is very slow at these concentrations

D. B & C

E. all of the above

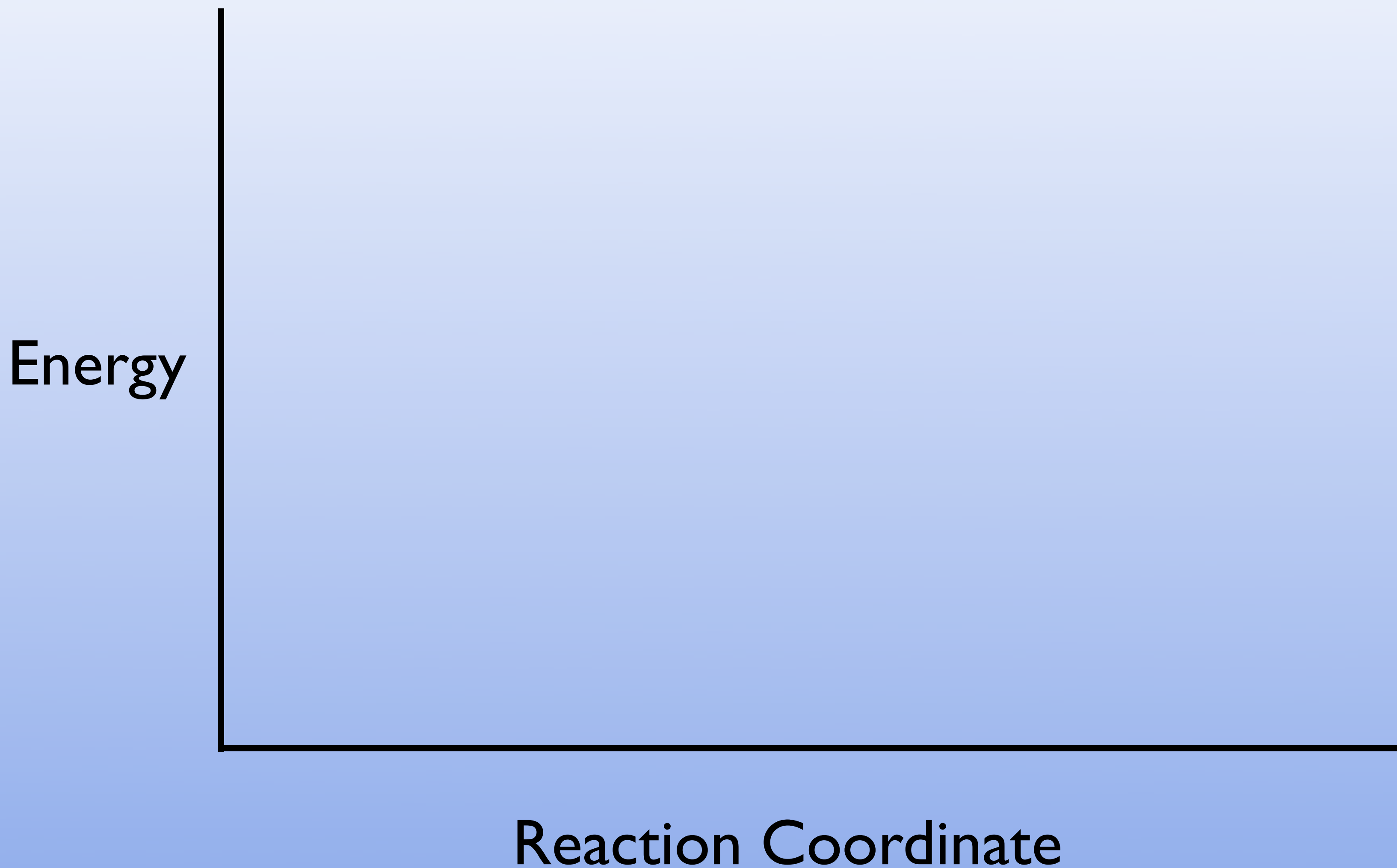

O
N
Br
O
N
Br
O
N
O
N
Br
Br
(a)
O
N
Br
Br
N
O
O
N
Br
Br
N
O
(b)
Br
N
O
O
N
Br
Br
N
O
O
N
Br
No reaction
(c)

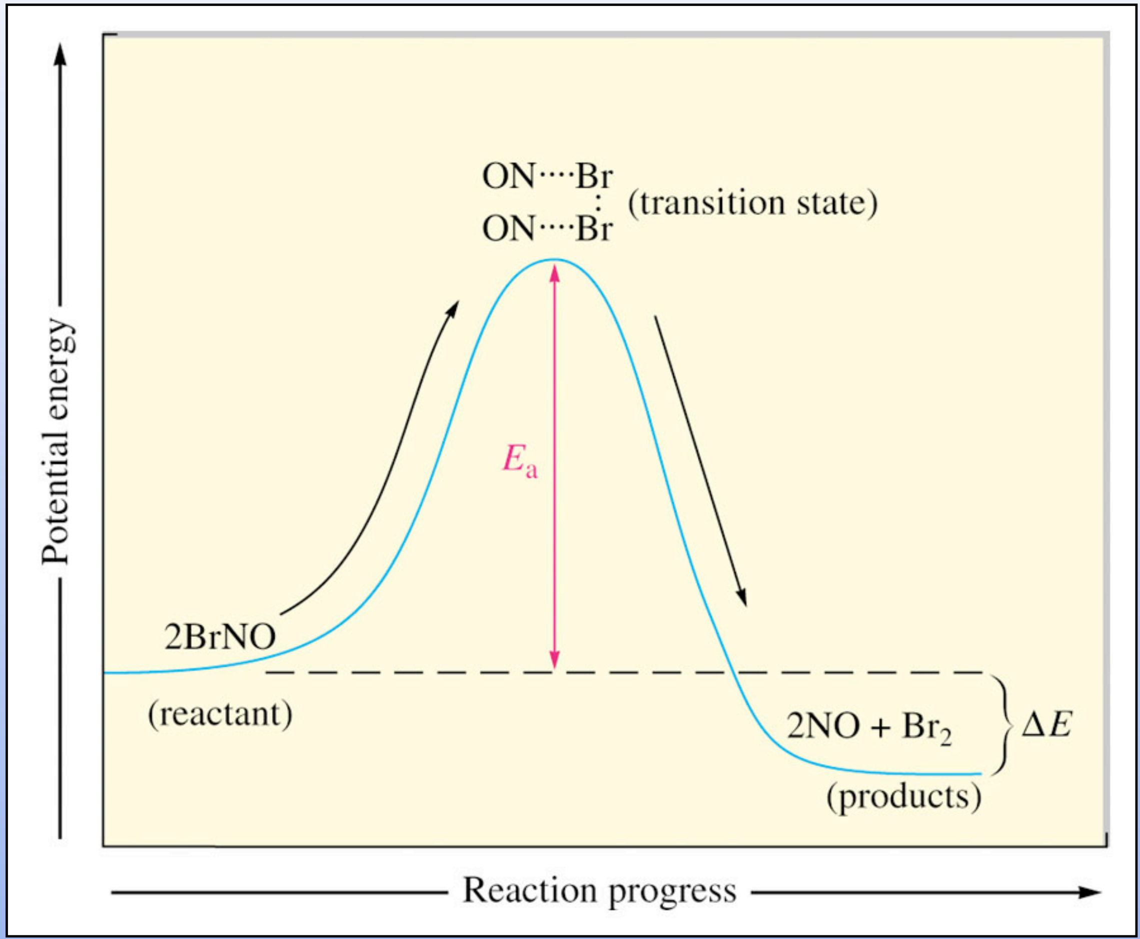
When the reaction is very very slow

the problem is typically that the rate constant is very small

What affects the rate constant?

Arrhenius Picture




ON····Br
ON····Br
(transition state)
Potential energy
E_a
2BrNO
(reactant)
$2NO + Br_2$
(products)
ΔE
Reaction progress

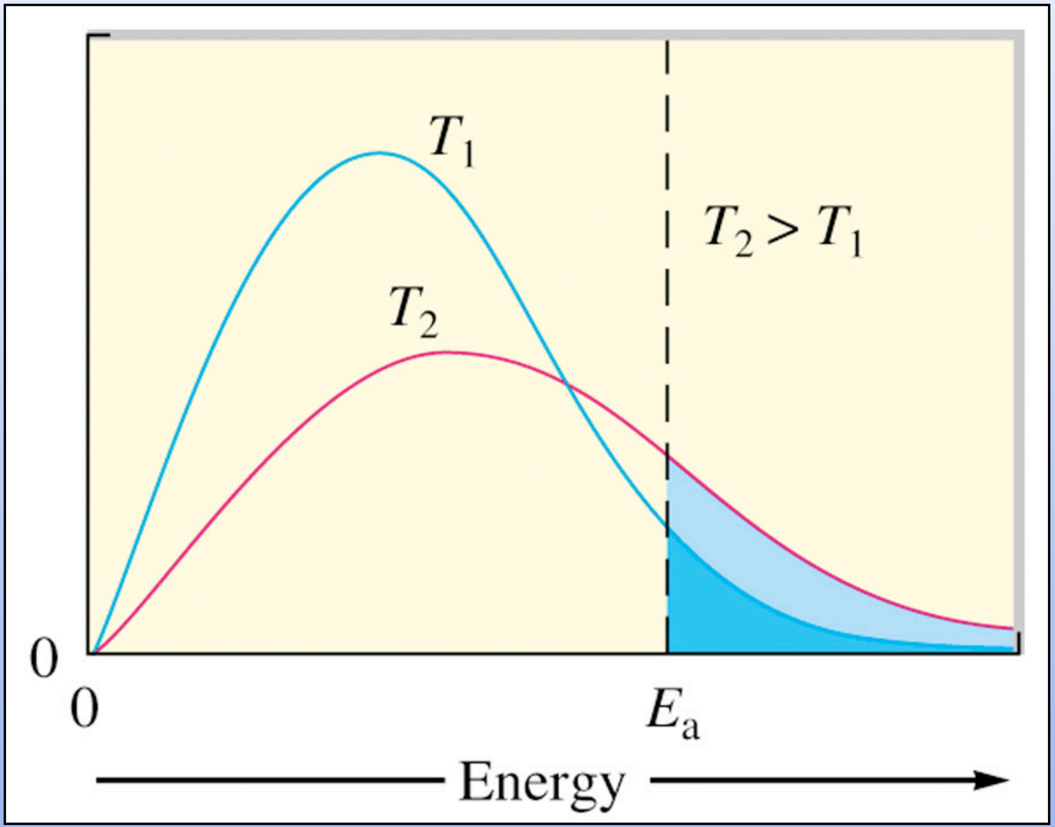
At a given temperature the molecules in a sample

A. all have the same energy

B. have a distribution of energies

C. have one of several fixed energies

How many molecules have enough energy to get over the barrier?



Arrhenius Law

The rate constant k is a function of temperature

pre-factor

barrier

$$k = A\, e^{-E_a/RT}$$

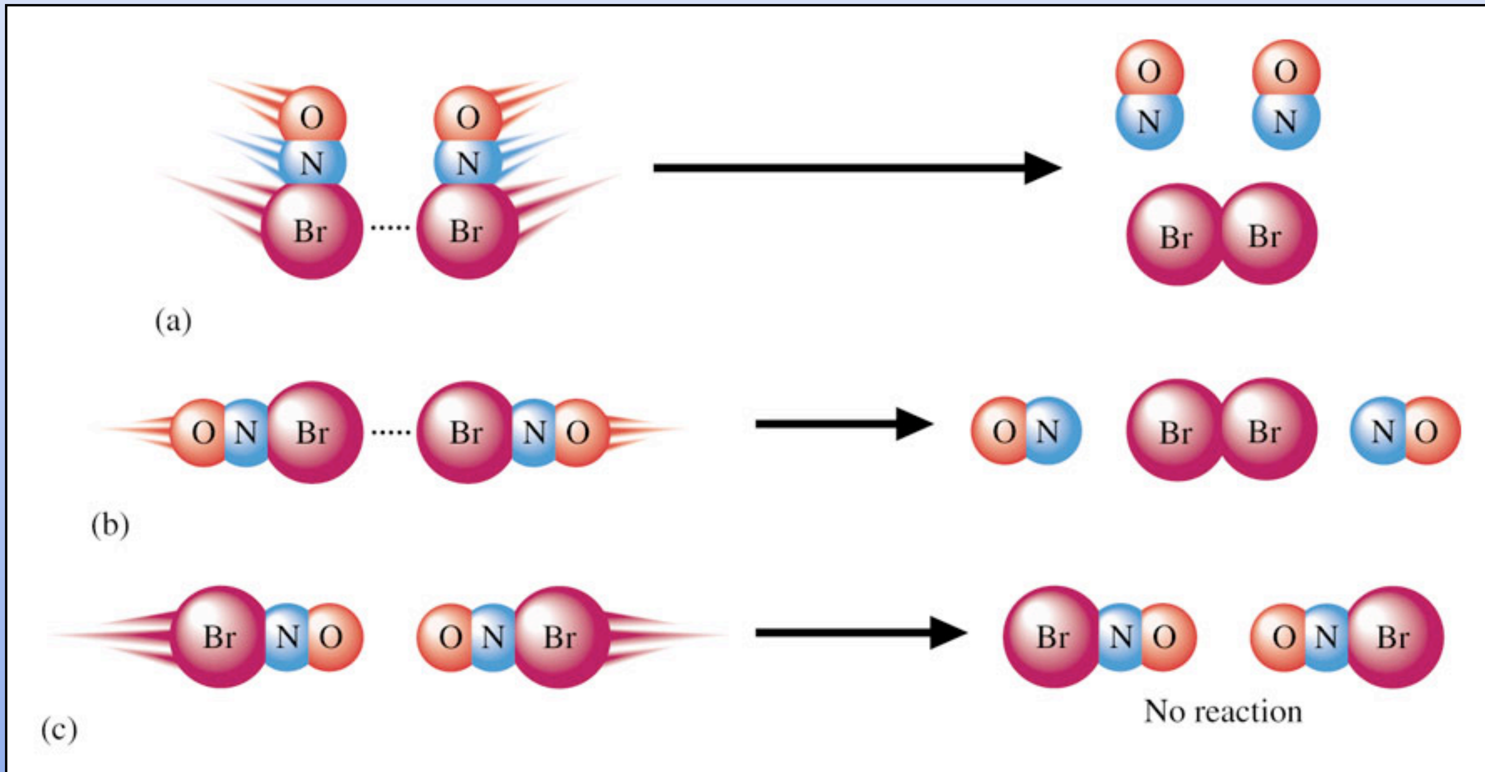
temperature

Arrhenius Law

The higher the temperature the more molecules that have enough energy to make it over the barrier

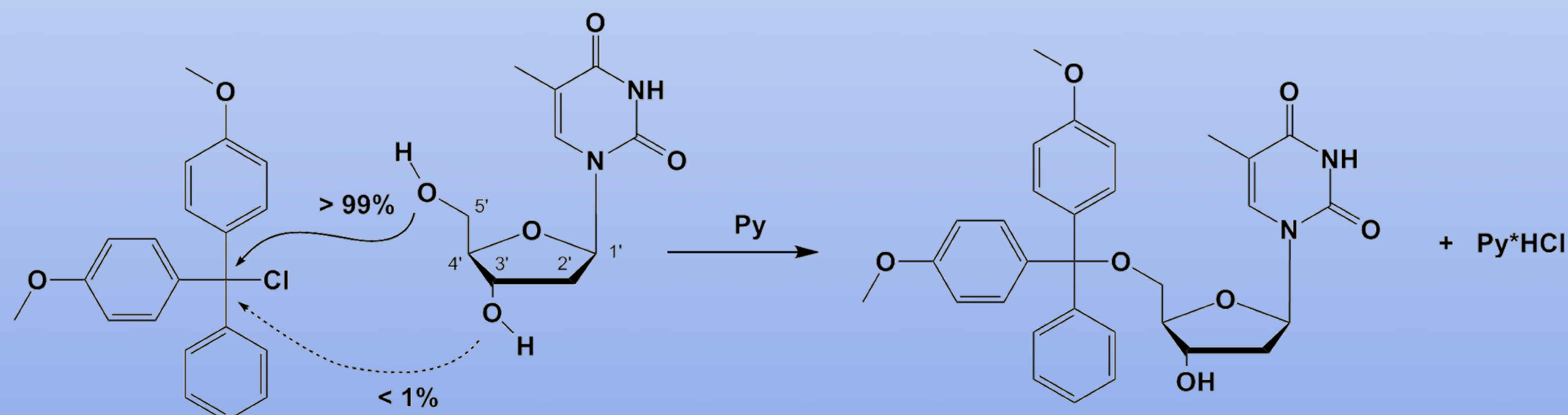
What is A?

This is the rate at infinite temperature
(not all interactions between the molecules
even with sufficient energy will lead to products)



Very important in organic chemistry
"steric effect"
"steric hindrance"
"steric protection"

putting a big unreactive part of the molecule
"in the way"
to slow (or stop) the reaction



Let's make a new Equation

$$k = A\ e^{-Ea/RT} \qquad \ln k = \ln A - E_a/RT$$

let's look at two temperatures

$$\ln k_1 = \ln A - E_a/RT_1$$
$$\ln k_2 = \ln A - E_a/RT_2$$

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let's look at two temperatures

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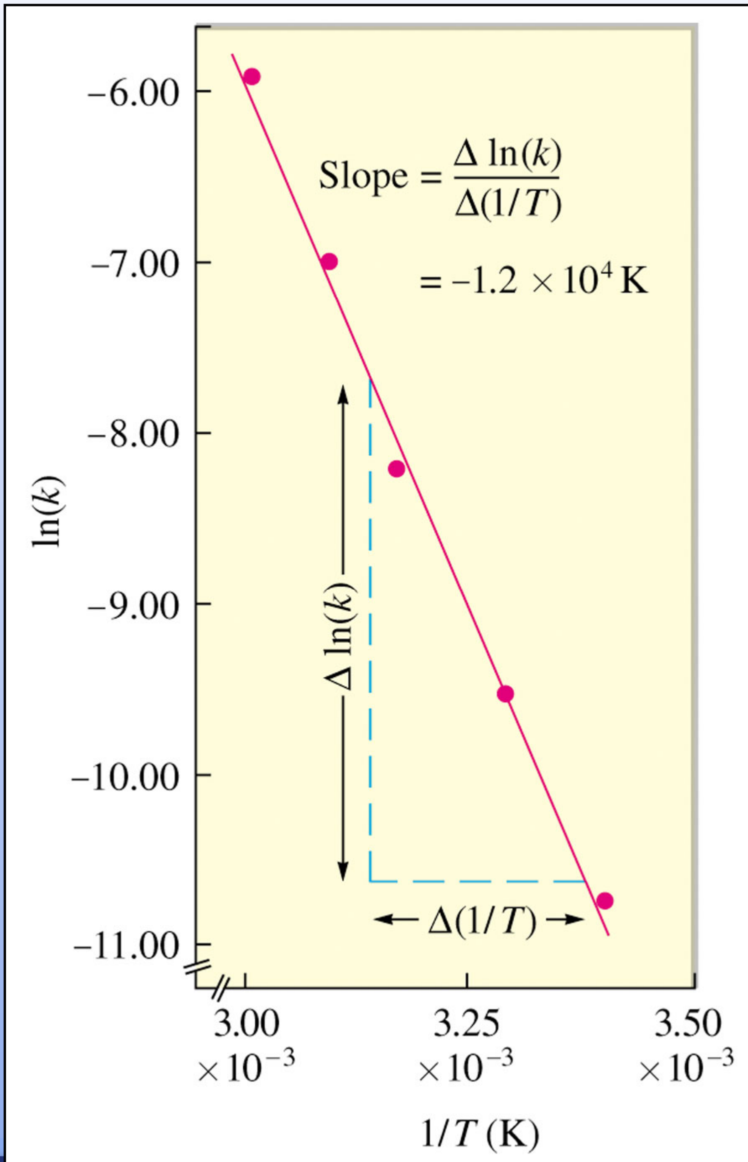
subtract to get a new equation that doesn't have A

$$\ln(k_2/k_1) = \frac{-E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$



The activation energy for this reaction is?

A. -1.2×10^4 K

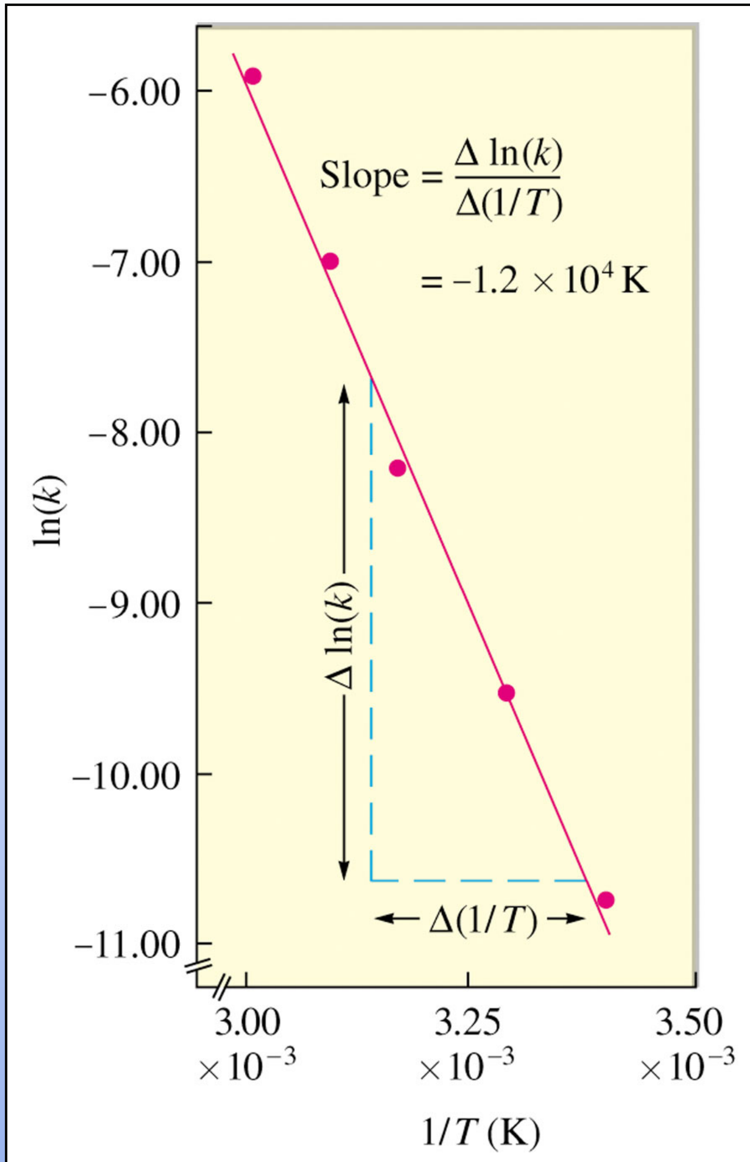
B. 1×10^5 J mol^{-1}

C. 1.2×10^4 J mol^{-1}

D. 1×10^5 K

E. -1×10^2 kJ mol^{-1}

$$\ln(k_2/k_1) = \frac{-E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$



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E. -1×10^2 kJ mol^{-1}

Slope = $-E_a/R$

$E_a = -R \times$ slope

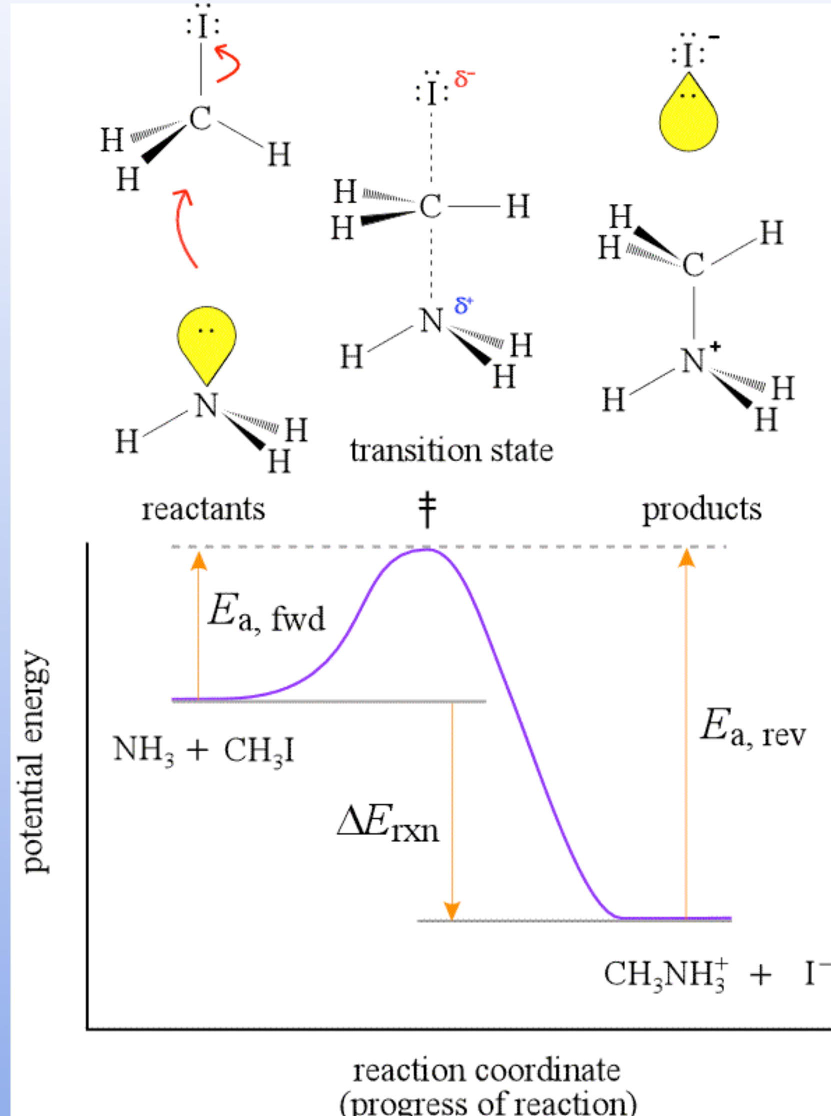
$E_a = -8.314$ J K^{-1} $mol^{-1} \times (-1.2 \times 10^4$ K$) = 1 \times 10^5$ J mol^{-1}

Why are reactions faster at higher temperatures?

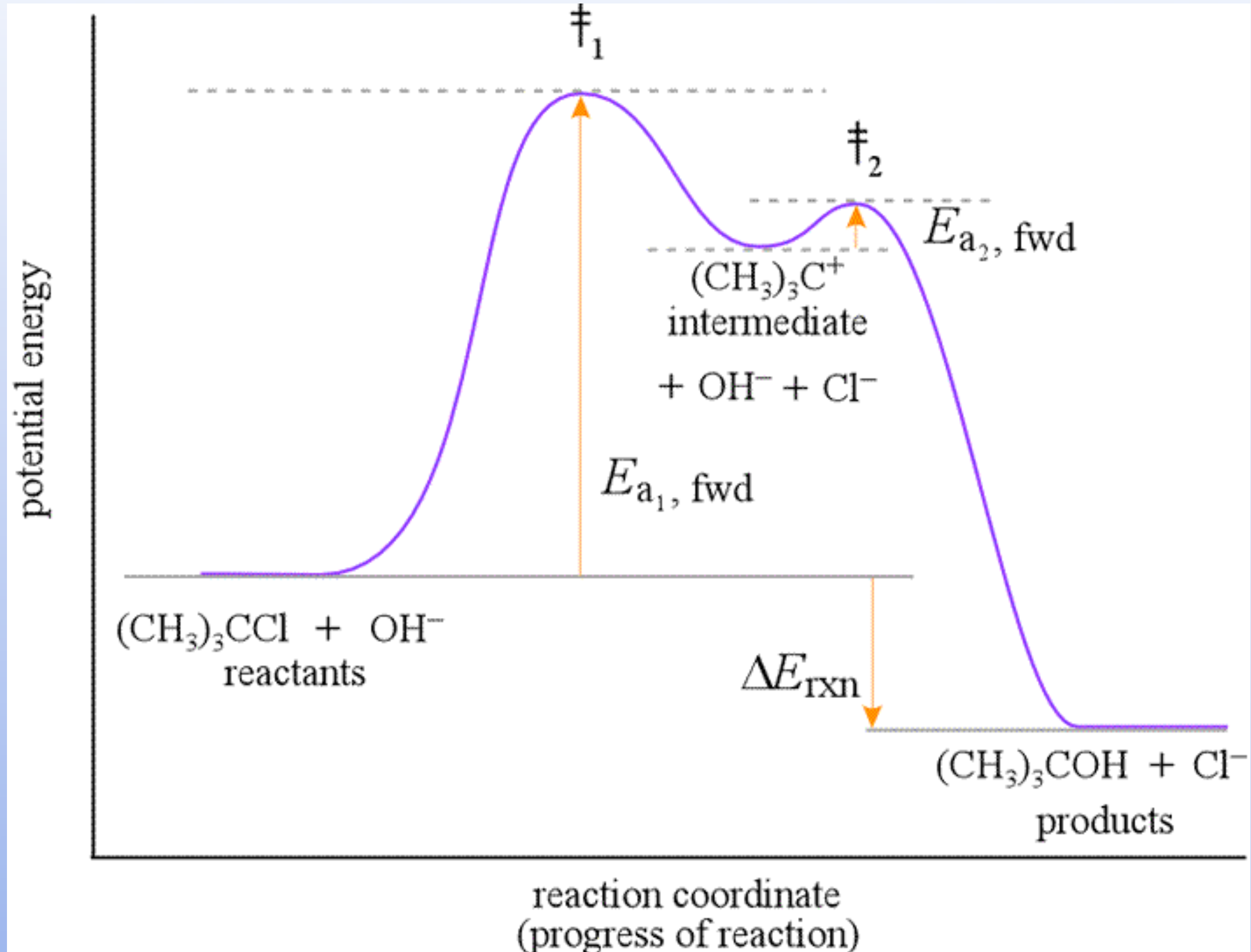
More molecules have sufficient energy to get over the barrier. BIG EFFECT

More molecules have collisions (but this is a very small effect) that is ignored in Arrhenius view

Transition State Theory

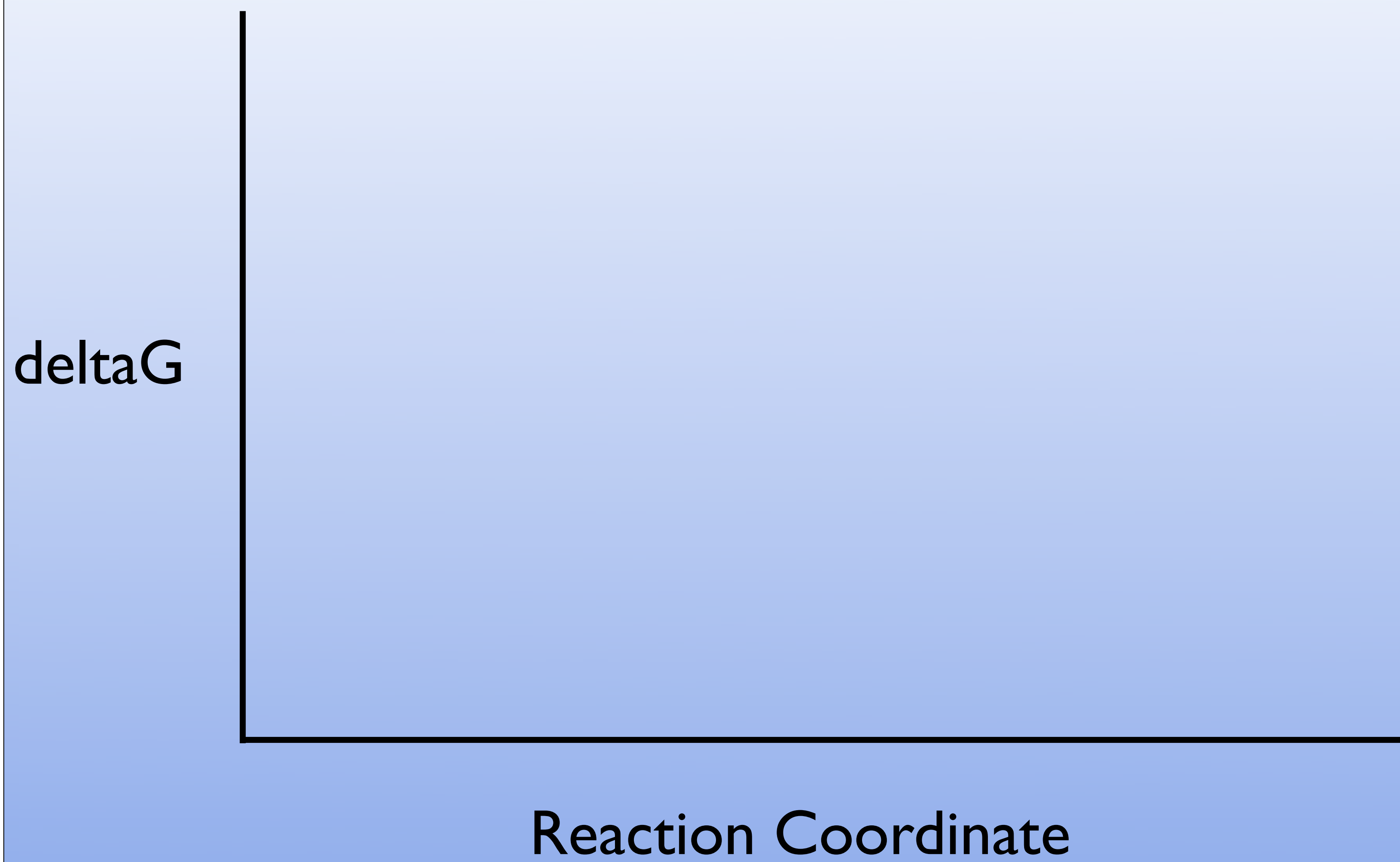


Transition State Theory



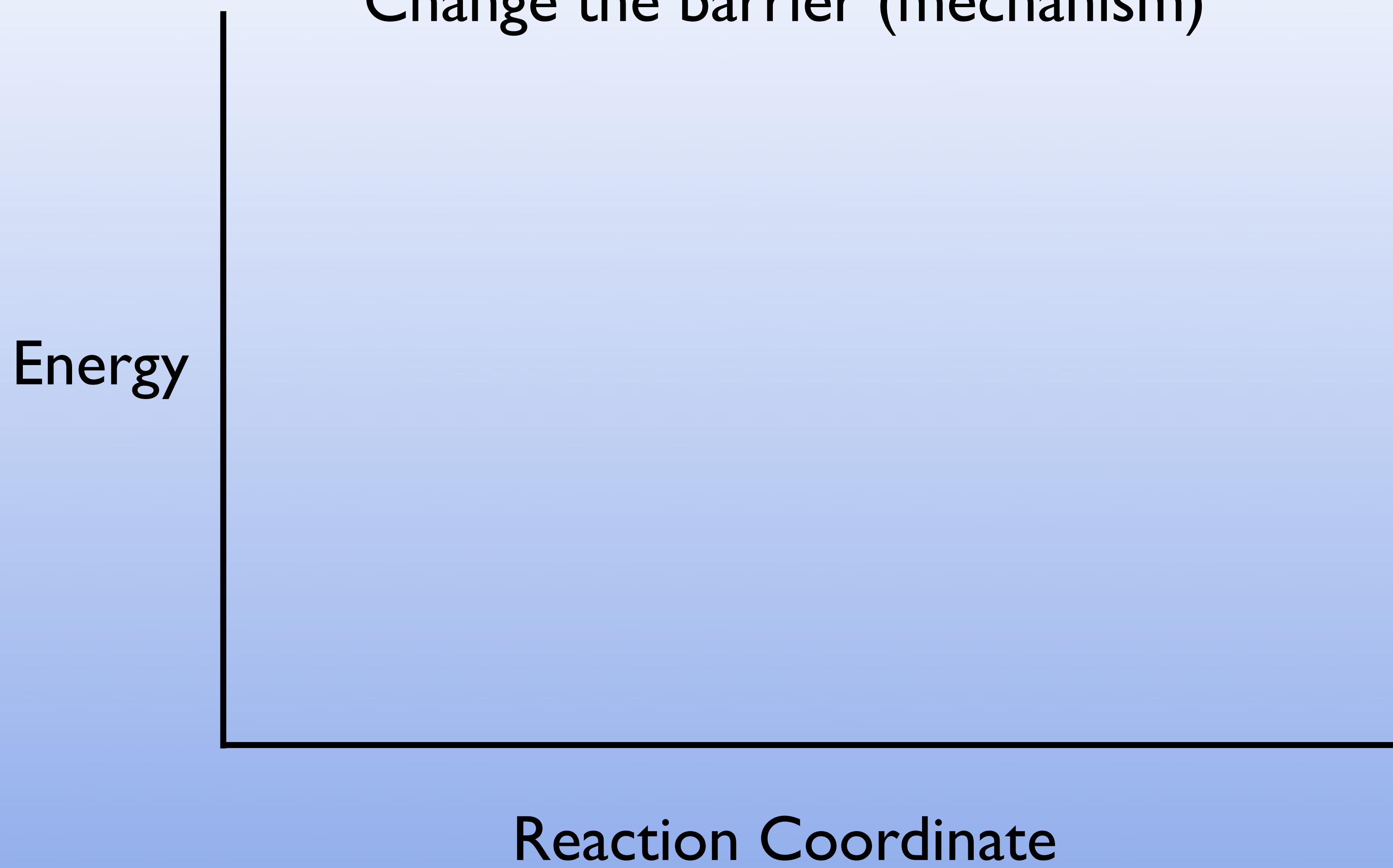
Two Step Mechanism (Two Barriers)

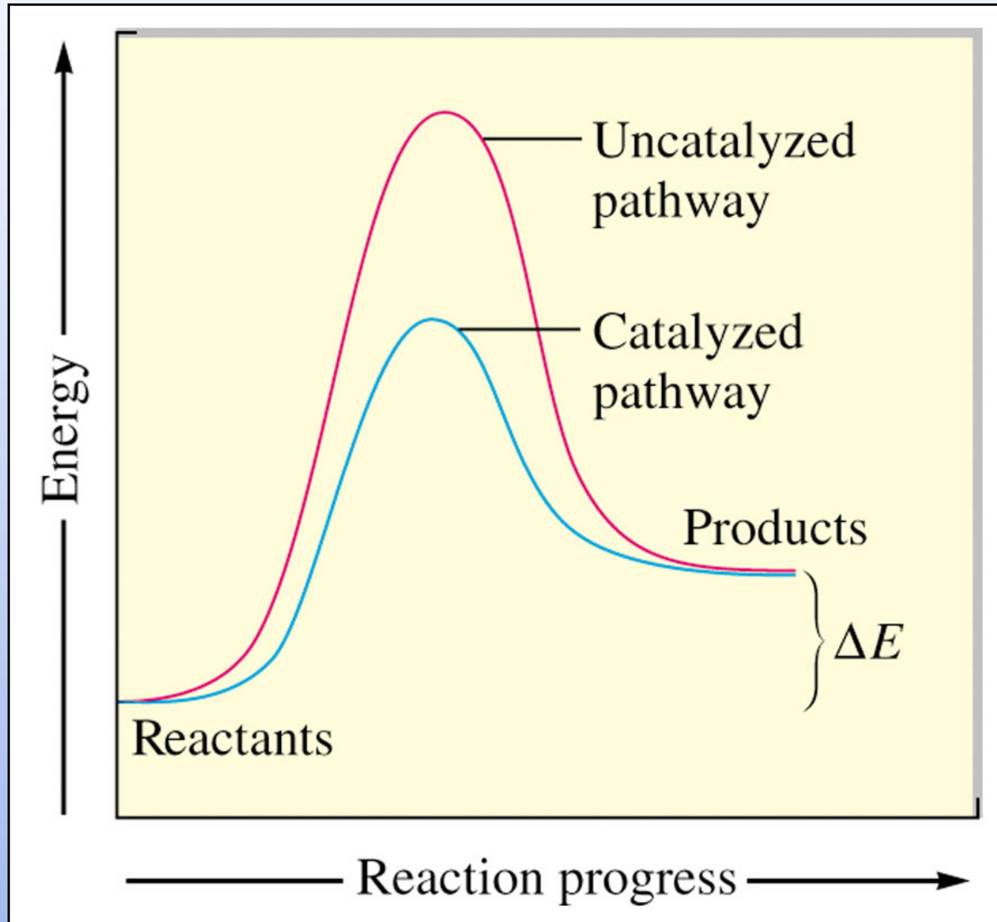
What is the rate limiting step?
We need to write reaction coordinate vs Free Energy



How else can affect k?

Change the barrier (mechanism)




Energy
Uncatalyzed pathway
Catalyzed pathway
Products
ΔE
Reactants
Reaction progress

Catalyst

Lower the barrier for the reaction
(by changing the mechanism)

Is not consumed during the course of the reaction
(it can be used over and over again)

However, it might under go chemistry during the reaction,
but the original form is regenerated by reaction.

Decomposition of Hydrogen Peroxide

$$H_2O_2(l) \longrightarrow O_2(g) \quad + \quad H_2O(l)$$

This reaction is very slow at room temperature
(thus you can get a bottle of H_2O_2 at the store)

demo

What happens when I add the catalyst

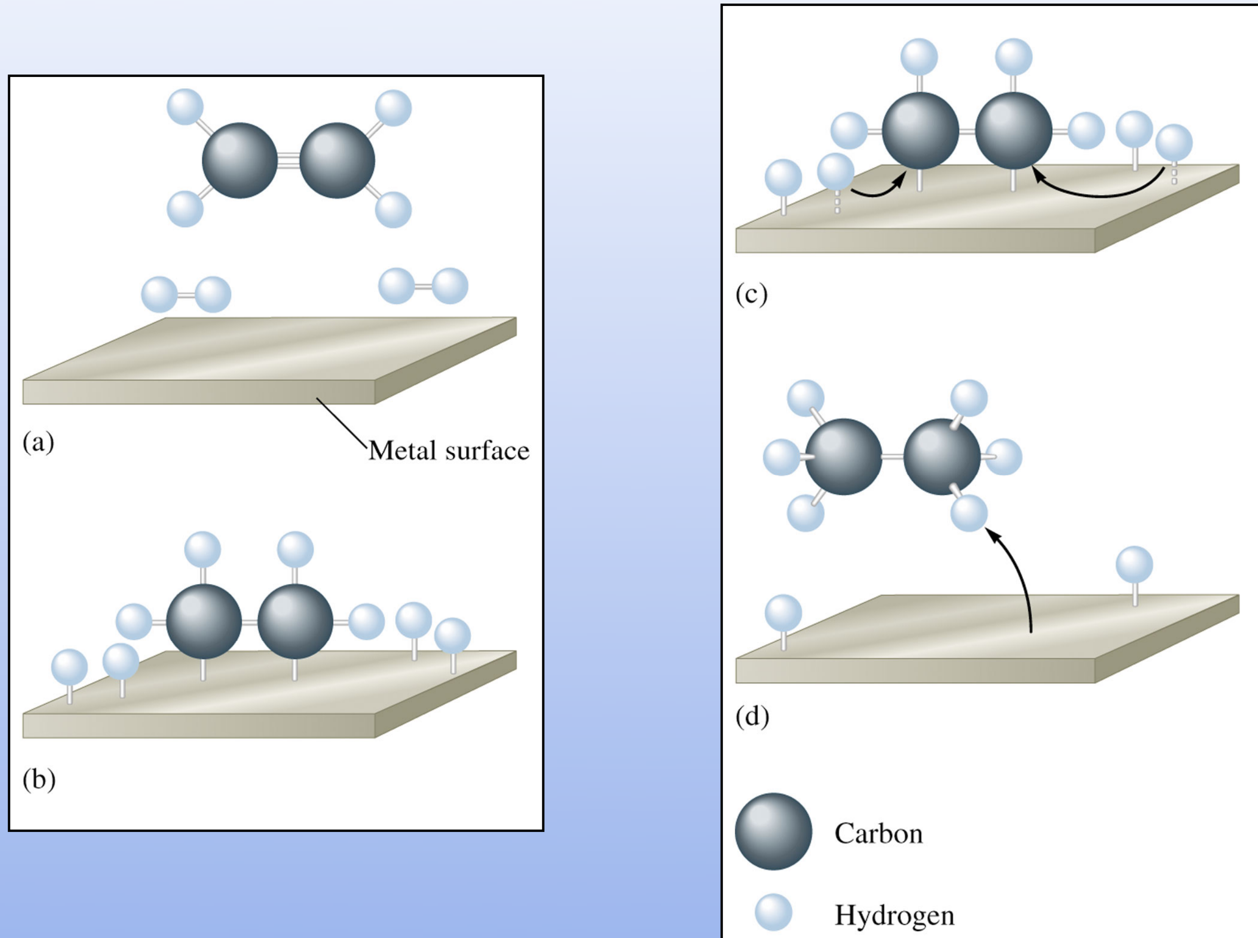
$$H_2O_2 + MnO_2 + 2H^+ \longrightarrow Mn^{2+} + 2H_2O + O_2$$

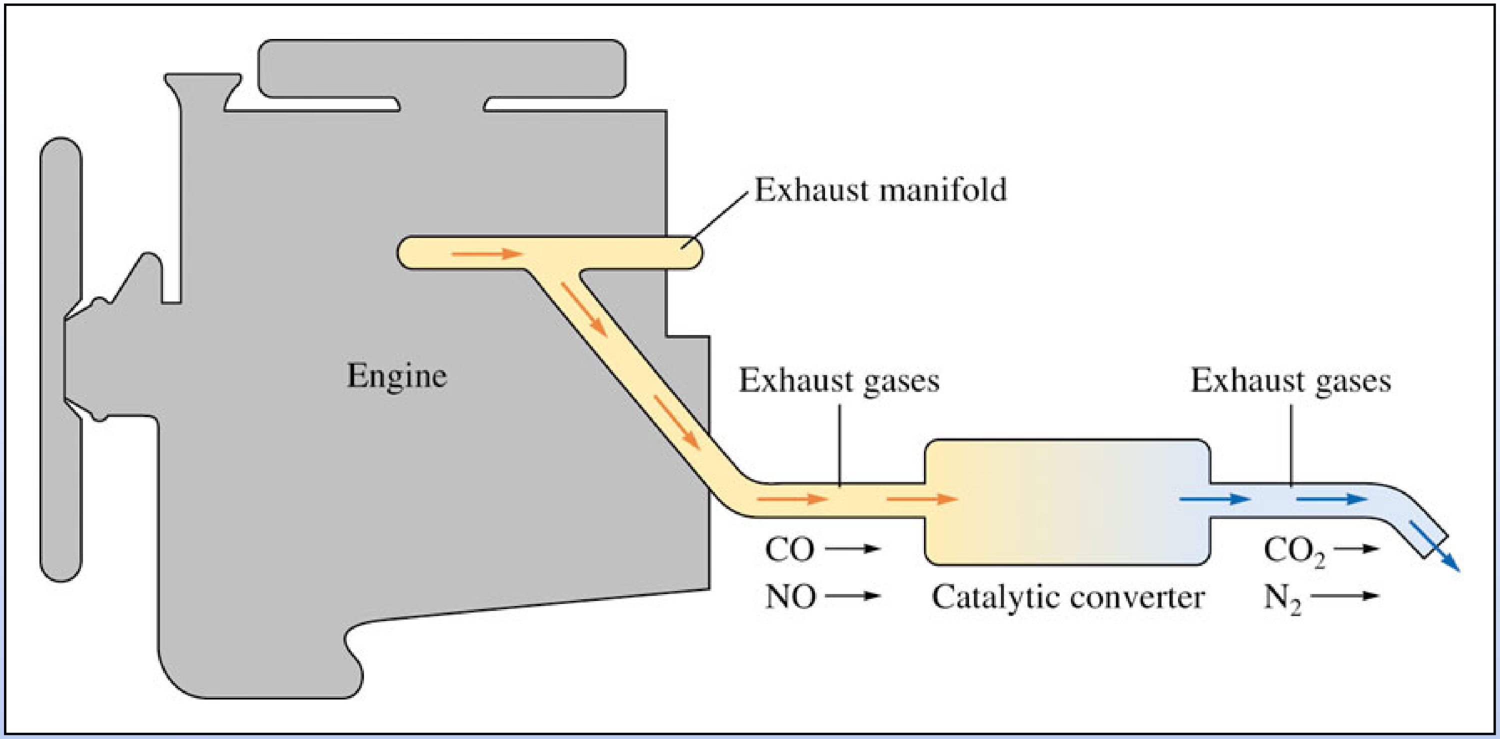
$$Mn^{2+} + 2H_2O_2 \longrightarrow Mn(OH)_2 + 2H^+$$

$$Mn(OH)_2 + H_2O_2 \longrightarrow MnO_2 + 2H_2O$$

Note: During the reaction the catalyst changes.
But at the end it is back to the same compound!

How do many catalysts work?





Catalyzes three chemical reactions

$$2NO_x \longrightarrow xO_2 + N_2$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$2C_xH_y + (2x+y/2)O_2 \longrightarrow 2xCO_2 + yH_2O$$

Haber Process (Fritz Haber Nobel 1918)
Formation of Ammonia

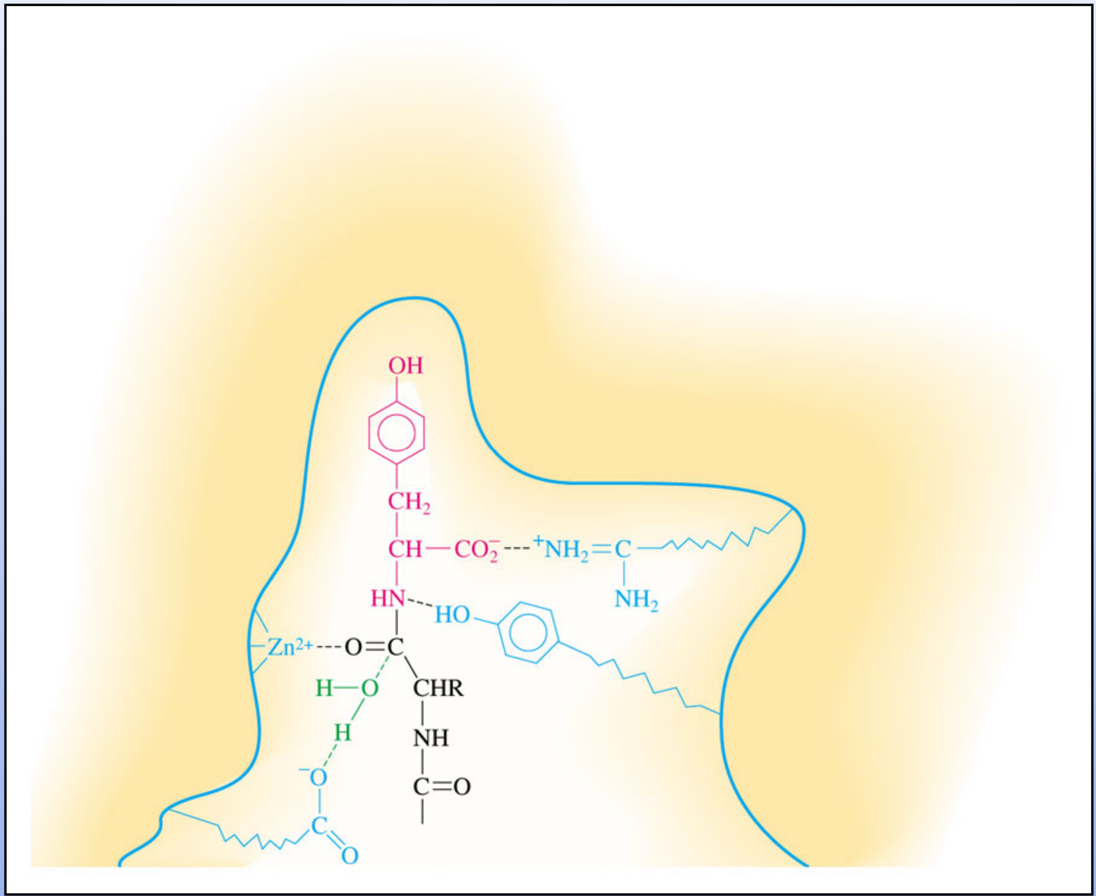
1. $N_2(g) \rightarrow N_2(\text{adsorbed})$
2. **$N_2(\text{adsorbed}) \rightarrow 2N(\text{adsorbed})$**
3. $H_2(g) \rightarrow H_2(\text{adsorbed})$
4. $H_2(\text{adsorbed}) \rightarrow 2H(\text{adsorbed})$
5. $N(\text{adsorbed}) + 3H(\text{adsorbed}) \rightarrow NH_3(\text{adsorbed})$
6. $NH_3(\text{adsorbed}) \rightarrow NH_3(g)$

originally osmium and uranium

Now iron (keep out the O_2)

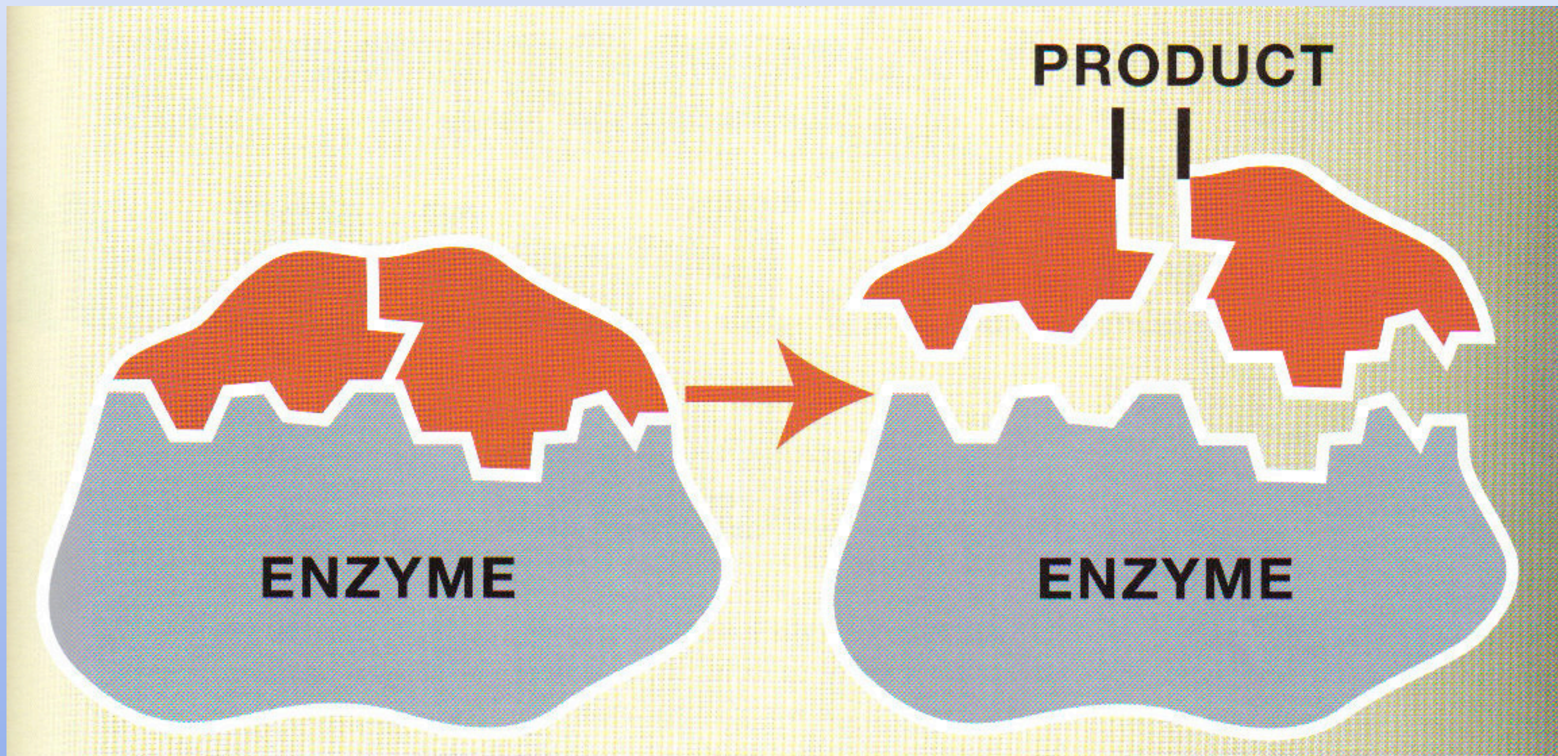
Ertl Nobel Prize 2008

Enzymes
Biological Catalysts



Substrate + Enzyme = Complex = Product + Enzyme

S + E = [SE] = P + E



Enzyme   Name = Function

Glucose Oxidase
Oxidizes Glucose

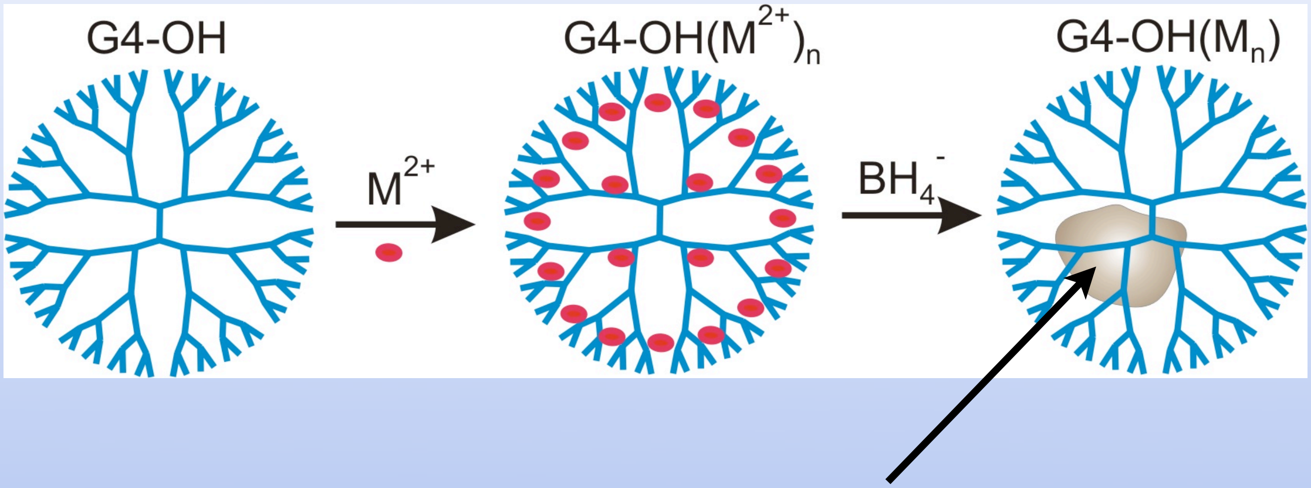
Aromatic Amine Dehydrogenase
removes Hydrogen from an aromatic amine

Hydrolase   Hydrolyze reactions

Isomerase   Isomerize molecules

Transferase   Transfers functional groups

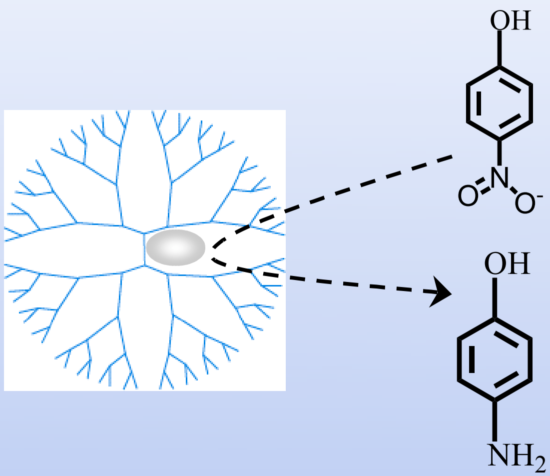
Freshman Research Initiative Project
Nanomaterials

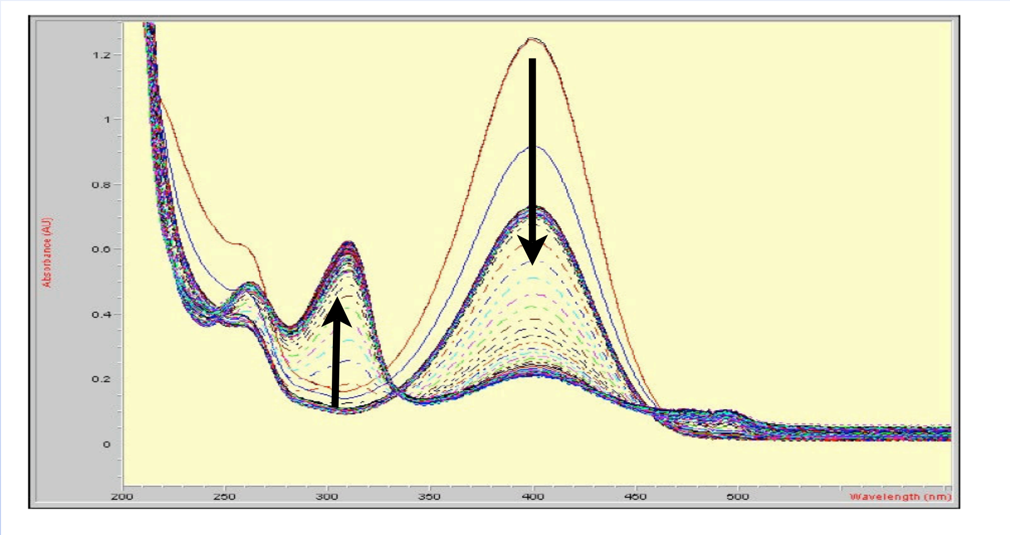


Dendrimer encapsulated nanoparticle

small metal particle
can be made of a variety of materials
(Au,Ag, Pd, Pt, Cu, Pt/Cu, Pd/Cu,....)

How good is the catalyst? Measure the kinetics

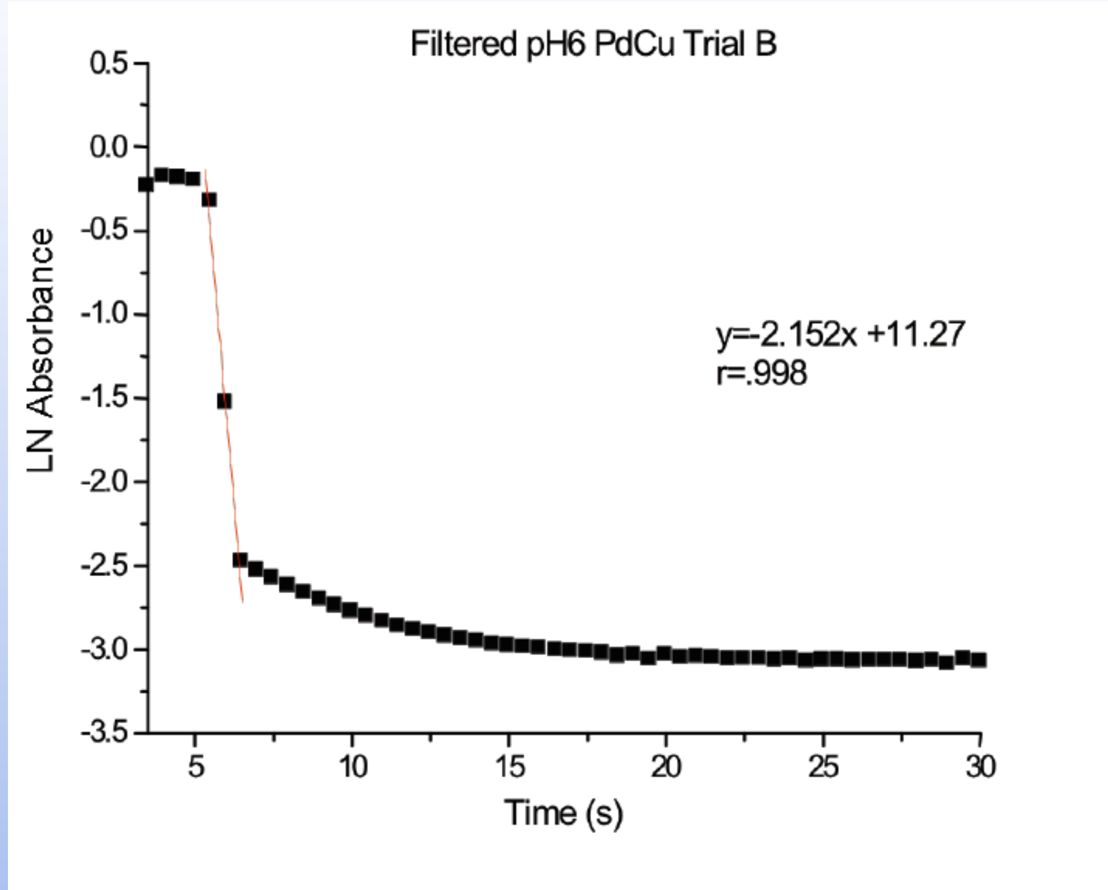




Measure the concentration as a function of time.

Kinetics are first order in reactant

plot   ln[concentration] vs time   slope = -k



Kinetics Wenly Ruan, Alex Guevaraal 2007